



Structures of Two Diastereomeric Aldol Products from a New Silicon-Directed Condensation

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des groupes morpholino varient de 1,627 à 1,662 Å; on remarquera que ces valeurs sont plus grandes que celles des liaisons P—N du cycle phosphazène (1,574 à 1,612 Å). Les quatre groupes morpholino sont en configuration chaise. Cette configuration est fortement déformée dans le cas du groupe morpholino défini par les atomes N4, C1, C2, O1, C3 et C4. Les groupes morpholino en configuration chaise (Fig. 1) sont signalés par Romming & Songstrad (1979) et Sarkar & Gupta (1980). La projection de la structure sur le plan yOz parallèlement à a (Fig. 2) permet de mettre en évidence les différentes possibilités de polymérisation. Elle est possible lorsqu'on substitue deux atomes de chlore par une diamine. Deux sortes de chaînes se développent entre les atomes de phosphore notés P1 et P2. Ces chaînes sont parallèles soit au plan xOy soit au plan xOz . Les valeurs des dis-

tances entre ces atomes de phosphore varient de 6,565 à 9,800 Å. Le développement de ce réseau dans l'espace conduit à un polymère tri-dimensionnel.

Références

- ALLCOCK, H. R., GREIGER, P. P., WAGNER, L. J. & BERNHEIM, M. Y. (1981). *Inorg. Chem.* **20**, 716–722.
 MUKHINA, L. E. & KROPACHEVA, A. A. (1966). *J. Gen. Chem. USSR*, **38**, 314–317.
 ROMMING, C. & SONGSTRAD, J. (1979). *Acta. Chem. Scand. Ser. A*, **33**(3), 187–197.
 RUTH, J. S., PARVEZ, M. & ALLCOCK, H. R. (1986). *J. Am. Chem. Soc.* **108**, 6089–6090.
 SARKAR, P. B. & GUPTA, S. P. (1980). *Cryst. Struct. Commun.* **9**(4), 925–932.
 SHELDRICK, G. M. (1976). Program for crystal structure determination. Univ. de Cambridge, Angleterre.
 WALKER, N. & STUART, D. (1983). *Acta. Cryst.* **A39**, 158–166.

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Structures of Two Diastereomeric Aldol Products from a New Silicon-Directed Condensation

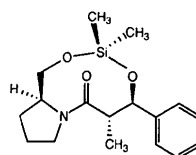
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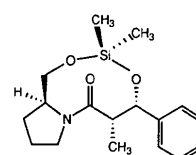
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Abstract. Hexahydro-3,3,6-trimethyl-5-phenyl-1*H*,7*H*-pyrrolo[2,1-*e*][1,3,6,2]dioxazasilonin-7-one, $C_{17}H_{25}NO_3Si$, $M_r = 319.48$. (2*S*,3*R*)-*anti*-Diastereomer (I), orthorhombic, $P2_12_12_1$, $a = 8.716$ (4), $b = 11.677$ (3), $c = 17.161$ (6) Å, $V = 1746$ (1) Å³, $Z = 4$, $D_x = 1.22$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 1.50$ cm⁻¹, $F(000) = 688$, room temperature, final $R = 0.040$ for 1683 reflections with $F_o^2 > 0$. (2*S*,3*S*)-*syn*-Diastereomer (II), monoclinic, $P2_1$, $a = 6.633$ (2), $b = 14.645$ (3), $c = 9.630$ (2) Å, $\beta = 109.96$ (2)°, $V = 879.3$ (4) Å³, $Z = 2$, $D_x = 1.21$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 1.49$ cm⁻¹, $F(000) = 344$, room temperature, final $R = 0.042$ for 2537 reflections with $F_o^2 > 0$. The compounds have a nine-membered heterocyclic ring containing the Si atom, the N atom of the pyrrolidine ring, two O atoms bonded to silicon and a carbonyl C atom. Bond distances in the molecules are normal and equivalent bonds are equal within three times their e.s.d.'s. Isomer (I) shows a disorder in the pyrrolidine ring that is absent in isomer (II).

Introduction. The silicon-bridged nine-membered ring aldol products (I) and (II) were formed in a new silicon-directed aldol condensation reaction (Myers



anti-Diastereomer (I)



syn-Diastereomer (II)

& Widdowson, 1990). These highly crystalline products were submitted to X-ray analysis to determine stereochemical assignments and to gain insight into the mechanism of the aldol addition reaction which forms them. The structures determined herein lend credence to the notion that (I) and (II) are formed in a reaction involving pentavalent silicon. In each structure, the amide carbonyl group lies over one face of the silicon-centered tetrahedron, in van der Waals contact with the Si atom. A transition state leading to this geometry that

* Contribution No. 8230.

involves trigonal bipyramidal silicon with methyl and enol substituents in the apical positions is easy to visualize.

Experimental. *Isomer (I).* Crystal an irregular cube, cut to 0.31 × 0.35 × 0.40 mm; CAD-4 diffractometer; ω -scan; 25 reflections with $14 < 2\theta < 18^\circ$ used to calculate cell dimensions; no absorption correction made ($\mu_{\text{rmax}} = 0.05$); $(\sin\theta/\lambda)_{\text{max}} = 0.60 \text{ \AA}^{-1}$; data collected for h from 0 to 10, k from 0 to 13 and l from -20 to 20; standard reflections 142, $\bar{1}16$ and $\bar{3}\bar{1}4$ showed no variations greater than predicted by counting statistics. 3500 reflections measured and merged to give 1773 unique reflections; goodness of fit for merging 0.98; R_{int} for merging 0.018 for 1551 reflections with exactly two observations; all reflections used in solution and refinement, including 90 for which $F_o^2 < 0$. Structure solved by *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) which gave coordinates of Si and 13 other atoms; remainder found by structure factor-difference map calculations; refinement used F_o^2 values; H atoms placed at calculated positions (C—H, 0.95 Å) and repositioned once, but not refined; final refinement included coordinates and anisotropic thermal parameters of all heavy atoms (except disordered C12AB, isotropic), scale factor, secondary-extinction parameters and population parameter for C12A (C12B population = 1 - C12A). For all 1683 reflections with $F_o^2 > 0$, $R = 0.040$, $wR = 0.006$; for 1536 reflections with $F_o^2 > 3\sigma(F_o^2)$, $R = 0.035$, $wR = 0.005$, $S = 2.21$ for 1773 reflections and 200 parameters; variances of the individual reflections assigned based on counting statistics plus an additional term, $(0.014I)^2$; variances of the merged reflections determined by standard propagation of error plus another additional term $(0.014I)^2$; $w = 1/[\sigma^2(F_o^2)]$; max. shift/e.s.d. in final least-squares cycle, 0.10 for C12AB, 0.01 for all other parameters; max. and min. heights in final difference Fourier map +0.25 and -0.19 e Å⁻³; secondary-extinction parameter (Larson, 1967) refined to $8.7(3) \times 10^{-6}$. Atomic scattering factors taken from Cromer & Waber (1974); dispersion corrections from Cromer (1974); programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964), *MULTAN* (Main *et al.*, 1980) and *ORTEP* (Johnson, 1976). The population parameter for C12A refined to 0.45 (3), leaving C12B at 0.55.

Isomer (II). Crystal a roughly cubic chunk, 0.44 × 0.50 × 0.41 mm; CAD-4 diffractometer; ω -scans; 25 reflections with $13 < 2\theta < 20^\circ$ used to calculate cell dimensions; no absorption correction made ($\mu_{\text{rmax}} = 0.06$); $(\sin\theta/\lambda)_{\text{max}} = 0.70 \text{ \AA}^{-1}$; data collected for h from -9 to 9, k from -20 to 20 and l from 0 to 13; standard reflections $0\bar{2}\bar{3}$, $\bar{1}42$ and $\bar{1}\bar{5}0$ showed a slight (<0.5%) linear decay. 5485 reflections measured and

Table 1. *Final atomic coordinates ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^4$) for C₁₇H₂₅NO₃Si*

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Isomer (I)	x	y	z	U_{eq} or B
Si	517 (1)	3044 (1)	2935 (0.4)	494 (2)
O1	761 (2)	4208 (2)	3457 (1)	459 (4)
O2	-1282 (2)	2823 (2)	2703 (1)	595 (5)
C16	1291 (4)	1791 (3)	3448 (2)	732 (9)
C17	1432 (4)	3355 (3)	1995 (2)	741 (9)
C1	1056 (3)	4365 (2)	4273 (1)	439 (6)
C2	2298 (3)	5234 (2)	4378 (1)	434 (6)
C3	3522 (4)	5020 (3)	4866 (2)	572 (8)
C4	4630 (4)	5846 (3)	4996 (2)	703 (9)
C5	4526 (5)	6882 (3)	4636 (2)	750 (9)
C6	3330 (4)	7100 (3)	4135 (2)	735 (9)
C7	2226 (4)	6280 (2)	4004 (2)	572 (7)
C8	-447 (4)	4737 (2)	4683 (2)	470 (7)
C9	-244 (4)	4824 (3)	5561 (2)	632 (8)
C10	-1655 (4)	3853 (2)	4476 (2)	490 (7)
O3	-1645 (3)	2913 (2)	4804 (1)	671 (6)
N	-2631 (3)	4085 (2)	3890 (1)	556 (6)
C11	-2739 (4)	5157 (3)	3450 (2)	663 (8)
C12A	-3721 (14)	4689 (13)	2726 (8)	5.9 (4)*
C12B	-4115 (14)	5086 (12)	2973 (8)	7.1 (3)*
C13	-4514 (5)	3779 (4)	2945 (3)	1150 (15)
C14	-3504 (4)	3167 (3)	3529 (2)	758 (9)
C15	-2431 (4)	2281 (3)	3164 (2)	707 (9)
Isomer (II)				
Si	8618 (0.9)	4053	1548 (0.6)	451 (1)
O1	8309 (2)	2961 (1)	1809 (2)	468 (3)
O2	7386 (3)	4371 (1)	-160 (2)	561 (4)
C16	11546 (4)	4199 (2)	2122 (3)	608 (6)
C17	7415 (5)	4758 (2)	2640 (3)	722 (7)
C1	6304 (3)	2496 (2)	1413 (2)	419 (4)
C2	5941 (3)	2106 (2)	2758 (2)	431 (4)
C3	7598 (4)	2010 (2)	4095 (3)	547 (5)
C4	7240 (5)	1638 (2)	5307 (3)	648 (7)
C5	5220 (5)	1361 (2)	5202 (3)	658 (7)
C6	3562 (5)	1447 (2)	3891 (3)	662 (6)
C7	3903 (4)	1827 (2)	2664 (3)	544 (5)
C8	6271 (4)	1749 (2)	261 (3)	469 (5)
C9	7737 (5)	953 (2)	914 (3)	647 (6)
C10	6916 (4)	2226 (2)	-924 (2)	473 (5)
O3	8714 (3)	2133 (2)	-991 (2)	662 (4)
N	5526 (3)	2837 (1)	-1787 (2)	492 (4)
C11	3231 (4)	2916 (3)	-2060 (3)	797 (8)
C12	2461 (5)	3483 (3)	-3452 (4)	904 (9)
C13	4271 (5)	4120 (2)	-3315 (3)	811 (8)
C14	6292 (4)	3578 (2)	-2514 (3)	558 (6)
C15	8020 (4)	4133 (2)	-1393 (3)	610 (6)

* Isotropic displacement parameter, B (Å²).

merged to give 2661 unique reflections; goodness of fit for merging 1.02; R_{int} for merging 0.019 for 2200 reflections with exactly two observations; all reflections used in solution and refinement, including 124 for which $F_o^2 < 0$. Structure solved by *MULTAN* (Main *et al.*, 1980) which gave the coordinates of Si and nine other atoms, the remainder being located by structure factor-Fourier synthesis calculations; refinement used F_o^2 values; H atoms were placed at calculated positions (C—H = 0.95 Å) assuming staggered geometry and repositioned once but not refined; final refinement included coordinates and anisotropic thermal parameters for all heavy atoms (y coordinate of Si held constant to fix the origin) and a scale factor. For all 2537 reflections with $F_o^2 > 0$, $R = 0.042$ and $wR = 0.007$; for 2239 reflections with $F_o^2 > 3\sigma(F_o^2)$, $R = 0.036$ and $wR = 0.006$; $S =$

Table 2. Distances (Å) and angles (°) not involving H atoms for $C_{17}H_{25}NO_3Si$

Isomer (I)

Si—O1	1.642 (2)	C8—C9	1.520 (4)
Si—O2	1.638 (2)	C8—C10	1.517 (4)
Si—C16	1.837 (4)	C10—O3	1.234 (3)
Si—C17	1.836 (3)	C10—N	1.344 (4)
O1—C1	1.435 (3)	N—C11	1.466 (4)
O2—C15	1.425 (4)	N—C14	1.454 (4)
C1—C2	1.495 (4)	C11—C12A	1.604 (14)
C1—C8	1.549 (4)	C11—C12B	1.454 (13)
C2—C3	1.380 (4)	C12A—C12B	0.715 (19)
C2—C7	1.381 (4)	C12A—C13	1.322 (14)
C3—C4	1.382 (5)	C12B—C13	1.566 (14)
C4—C5	1.362 (5)	C13—C14	1.514 (6)
C5—C6	1.374 (5)	C14—C15	1.529 (5)
C6—C7	1.376 (5)		

O2—Si—O1	112.8 (1)	C9—C8—C1	111.8 (2)
C16—Si—O1	110.5 (1)	C10—C8—C1	106.8 (2)
C17—Si—O1	105.1 (1)	C10—C8—C9	111.0 (2)
C16—Si—O2	110.0 (1)	O3—C10—C8	119.6 (3)
C17—Si—O2	103.5 (1)	N—C10—C8	118.5 (2)
C17—Si—C16	114.8 (2)	N—C10—O3	121.6 (3)
C1—O1—Si	131.4 (2)	C11—N—C10	126.8 (2)
C15—O2—Si	127.4 (2)	C14—N—C10	120.1 (3)
C2—C1—O1	109.5 (2)	C14—N—C11	112.1 (2)
C8—C1—O1	109.1 (2)	C12A—C11—N	98.2 (5)
C8—C1—C2	111.6 (2)	C12B—C11—N	107.1 (6)
C3—C2—C1	120.7 (2)	C13—C12A—C11	109.5 (9)
C7—C2—C1	120.8 (2)	C13—C12B—C11	104.8 (8)
C7—C2—C3	118.5 (3)	C14—C13—C12A	105.3 (7)
C4—C3—C2	120.8 (3)	C14—C13—C12B	108.1 (6)
C5—C4—C3	120.0 (3)	C13—C14—N	103.8 (3)
C6—C5—C4	119.9 (3)	C15—C14—N	110.7 (3)
C7—C6—C5	120.2 (3)	C15—C14—C13	113.9 (3)
C6—C7—C2	120.5 (3)	C14—C15—O2	110.9 (3)

Isomer (II)

Si—O1	1.643 (2)	C5—C6	1.368 (4)
Si—O2	1.635 (2)	C6—C7	1.392 (4)
Si—C16	1.841 (3)	C8—C9	1.511 (4)
Si—C17	1.839 (3)	C8—C10	1.518 (3)
O1—C1	1.425 (3)	C10—O3	1.224 (3)
O2—C15	1.432 (3)	C10—N	1.348 (3)
C1—C2	1.508 (3)	N—C11	1.459 (4)
C1—C8	1.553 (3)	N—C14	1.473 (3)
C2—C3	1.385 (3)	C11—C12	1.510 (5)
C2—C7	1.385 (3)	C12—C13	1.490 (5)
C3—C4	1.380 (4)	C13—C14	1.522 (4)
C4—C5	1.370 (4)	C14—C15	1.515 (4)

O2—Si—O1	112.7 (1)	C6—C7—C2	120.0 (2)
C16—Si—O1	103.9 (1)	C9—C8—C1	113.3 (2)
C17—Si—O1	111.0 (1)	C10—C8—C1	105.9 (2)
C16—Si—O2	112.5 (1)	C10—C8—C9	111.2 (2)
C17—Si—O2	104.5 (1)	O3—C10—C8	121.2 (2)
C17—Si—C16	112.5 (1)	N—C10—C8	117.4 (2)
C1—O1—Si	125.3 (1)	N—C10—O3	121.0 (2)
C15—O2—Si	125.3 (2)	C11—N—C10	128.0 (2)
C2—C1—O1	111.1 (2)	C14—N—C10	120.5 (2)
C8—C1—O1	108.2 (2)	C14—N—C11	111.3 (2)
C8—C1—C2	112.3 (2)	C12—C11—N	102.7 (3)
C3—C2—C1	121.9 (2)	C13—C12—C11	104.3 (3)
C7—C2—C1	119.6 (2)	C14—C13—C12	105.2 (3)
C7—C2—C3	118.5 (2)	C13—C14—N	103.8 (2)
C4—C3—C2	121.0 (2)	C15—C14—N	110.9 (2)
C5—C4—C3	120.0 (3)	C15—C14—C13	113.8 (2)
C6—C5—C4	119.9 (3)	C14—C15—O2	110.9 (2)
C7—C6—C5	120.5 (3)		

2.32 for 2661 reflections and 198 parameters; weights calculated as for isomer (I); max. shift/e.s.d. in final least-squares cycle < 0.005; max. and min. heights in the final difference map +0.22 and -0.17 e Å⁻³; no apparent need for secondary-extinction correction; scattering factors and computer programs as for isomer (I).

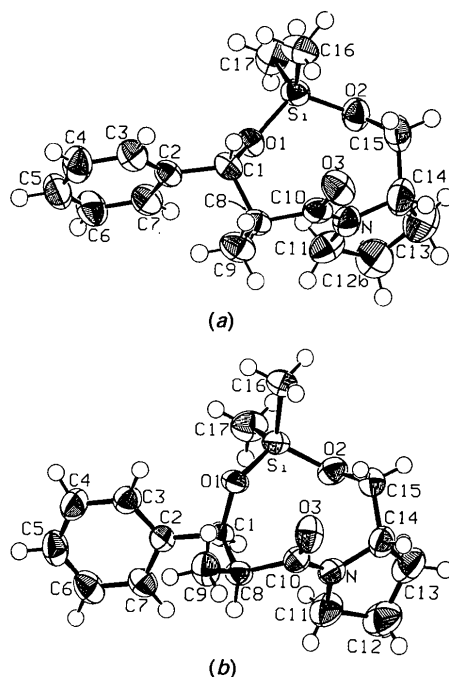


Fig. 1. An ORTEP drawing of (a) isomer (I) and (b) isomer (II) with 50% thermal ellipsoids. H atoms are shown as open spheres of arbitrary (small) dimension. (Atom C12A is not shown.)

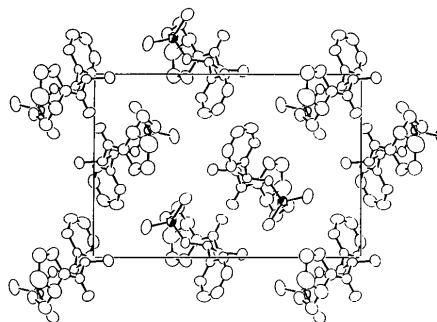


Fig. 2. An ORTEP projection of isomer (I), down the *a* axis; the *c* axis is vertical. A unit cell is outlined, the Si atom is shown shaded, H atoms are not shown, 50% thermal ellipsoids.

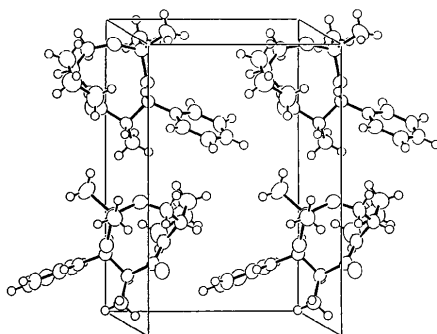


Fig. 3. An ORTEP projection of isomer (II) roughly perpendicular to the *bc* plane. One unit cell is outlined and the contents of two unit cells are shown. Heavy atoms are shown as 50% thermal ellipsoids, H atoms as arbitrary (small) spheres.

Final parameters are given in Table 1* for isomers (I) and (II).

Discussion. The two stereoisomers whose structures are described here show good similarities in bond distances and regular structures with no significant departures from expected bond lengths or angles. The disorder at C12 in isomer (I) makes comparisons in that region meaningless, but for the rest of the molecule these statements hold true (Table 2). The nine-membered ring has a certain amount of flexibility, but the two conformations, while differing at C1, are otherwise nearly equivalent. The carbonyl bond in both isomers exhibits normal van der Waals contacts across the ring: Si to the center of (C10, O3) is 3.56 Å in isomer (I) and 3.62 Å in isomer (II). We expected 3.55–3.65 Å based on data taken from Pauling (1960). The shortest (relatively speaking) contact we observed is Si—C10 = 3.39 Å in isomer (I); this is still approximately a van der Waals distance (radii for Si = 1.95, C = 1.50 Å).

In both structures the ketone O atom O3 has some contacts with H atoms on the benzene ring. In isomer (I) O3...H3 = 2.59 Å and in isomer (II) O3...H4 = 2.71 Å. These are not short enough to be considered as hydrogen bonds, but may indicate a

* Lists of structure factors, anisotropic thermal parameters, complete distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54215 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

small interaction between molecules in the crystal. Fig. 1 shows the numbering schemes for isomers (I) and (II). Figs. 2 and 3 show the packing of the isomers (I) and (II).

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References

- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DUCHAMP, D. J. (1964). Am. Crystallogr. Assoc. Meet., Bozeman, Montana, Paper B14, p. 29.
- JOHNSON, C. K. (1976). ORTEPII. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MYERS, A. G. & WIDDOWSON, K. L. (1990). *J. Am. Chem. Soc.* **112**, 9672–9674.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, NY: Cornell Univ. Press.

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Structure of a Chiral Cyclopentanone Precursor in Neocarzinostatin Synthetic Studies, C₂₀H₂₁NO₃S.H₂O

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Abstract. (1*E*,2*S*,3*R*)-2-[(4*R*,5*R*)-4,5-Dimethyl-1,3-dioxolan-2-yl]-3-(2-naphthylthio)cyclopentanone oxime, *M_r* = 373.47, orthorhombic, *P*2₁2₁1, *a* = 5.374 (13), *b* = 18.135 (3), *c* = 20.487 (5) Å, *V* = 1997 (5) Å³, *Z* = 4, *D_x* = 1.24 g cm⁻³, Mo *K*α, λ = 0.71073 Å, μ = 1.87 cm⁻¹, *F*(000) = 792, room tem-

perature, crystal volume 2.7 × 10⁻⁴ mm³, final *R* = 0.127 for 971 reflections with *F_o*² > 0 out of 1131 data, *R* = 0.065 for 467 reflections with *F_o*² > 3σ(*F_o*²). Despite the small crystal size (all larger crystals were twinned), a structural solution of adequate precision was obtained. Bond distances and angles in the molecule are normal; the water molecules are hydrogen bonded in a chain along the *a* axis and each

* Contribution No. 8229.